REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-01-

0528

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
September 10, 2001	FINAL	August 1, 1999 - July 31, 2001

4. TITLE AND SUBTITLE
Organic crystal films for electro-optic modulator

5a. CONTRACT NUMBER

5b. GRANT NUMBER
F49620-99-1-0308

5c. PROGRAM ELEMENT NUMBER

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5d. PROJECT NUMBER

5e. TASK NUMBER
1660/03

5f. WORK UNIT NUMBER

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University of Puerto Rico

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NL
801 N.Randolph St. Room 732
Arlington, VA 22203-1977

10. SPONSOR/MONITOR'S ACRONYM(S)
AFOSR/NL

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

13. SUPPLEMENTARY NOTES

14. ABSTRACT

During the period of performance from August 1st, 1999 to July 31st, 2001 the following was done: KD*P and N-(4-nitrophenyl)-(L)-prolinol (NPP) single crystals in longitudinal E-O modulator configuration have been studied. The E-O coefficient for KD*P, which is in good agreement with literature data, and electro-optical parameters for NPP were obtained. The latter are much higher that that received by other authors, which is explained by a substantial stress in the crystal due to the conversed piezoelectric effect. An E-O thin film modulator integrated with input and output coupling prisms was designed. Successful injection, propagation and decoupling light from the experimental prototype of the modulator were demonstrated. Applicability of different shape prisms for light coupling was explored. An opportunity to grow a thin organic film in a cell comprising a cell itself and a prism used as a lid, similar to the plate-guided method was studied.
Mr. Javier Wu defended his thesis "Nonlinear Optical Properties of Organic Thin Film Materials". Javier continues his studies in the Ph. D. program of the University of PR. Mr. Zhifu Liu defended his Ph.D. thesis "Electro-optical effect in single crystal films", and got a position with industry.

15. SUBJECT TERMS

20011026 013

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dr. Alexander Leyderman
N/A	N/A	N/A		16	19b. TELEPHONE NUMBER (include area code) (787)265-3844

Executive Summary

1. Introduction

Electro-optic devices, such as modulators and optical switches have a tremendous market. Currently, these devices are made of inorganic NLO material, such as lithium niobate ($LiNbO_3$) and potassium dihydrogen phosphate (KH_2PO_4). Organic materials have advantages over inorganic materials, which are particularly interesting. Organic materials based on extended π-electron systems have very large electro-optic coefficients. For example, the electro-optic coefficient r_{11} of 2-methyl-4-nitroaniline (MNA) is about twice as large as r_{33} of $LiNbO_3$[1]. Secondly, only electronic excitation contributes to second harmonic susceptibility of inorganic material, whereas electron and crystal vibration excitations contribute to Pockels effect. As pointed by Singer and Garito[2] the electro-optical switching time of an inorganic crystal would be limited to the characteristic times of crystal vibrations. However, the electronic contribution dominates both Pockels effect and second harmonic susceptibility in many organic materials. Thus the response time of an organic material would be much faster than that of an inorganic material. For example, the response time of MNA is expected to be 100 times faster than that of $LiNbO_3$. Thirdly, most organic materials have comparatively high damage thresholds. The last, but not least merit, is that organic materials are accessible to chemical modification.

However, in addition to having these merits, it is suggested that a good organic crystal should also posses adequate chemical, thermal and mechanical stability.[3] Generally speaking, molecule crystals lack mechanical strength and are highly susceptible to chemical attack, since the molecules are bound only by relatively weak Van der Waals forces. In our opinion, a molecular crystal film grown within a cell, which consists of two transparent quartz plates, can be well protected by the same cell[4]. If two plates are coated with transparent conductive layers, and a NLO crystal is grown between them, the system will form an electro-optic cell. We have reported successful fabrications of organic electro-optic cells with thin single crystals of meta-nitroaniline (mNA) and 2-cyclo-octylamino-5-nitropyridine (COANP) grown between two transparent plates, on which

indium-tin-oxide (ITO) layers were deposited (longitudinal configuration)[5,6]. The figures of merit for the two kinds of cells were medium due to the symmetry of the crystal, but the crystals were of high quality due to the excellent protection provided by the cells and the figure of merits of the crystals did not decrease with time[7]. With N-(4-nitrophenyl)-L-prolinol (NPP) crystals, we have prepared a Pockels cell with figure of merit as large as 98 pm/V.[8] With a few volts driving voltage, large modulation signals from the Pockels and Kerr cells were obtained.

In this proposal, we explored a variety of organic compounds to be used for fabrication of an electro-optic modulator using plate-guided (PG) method [4,6]. We also introduced a dielectric layer and an optical isolation layer to the electro-optic cell to form a planar wave-guide. Integrated with a prism coupler, the cell was developed as an electro-optic modulator. We designed and explored different prism shapes to optimize the light coupling into a waveguide.

2. Experimental Part

2-1. Thin crystalline film fabrication. Thin films were grown by the PG method[9,10]. This approach has such advantages as full control over the thickness of the film and selection of a proper seed for initial crystal growth. Fig. 1 shows the schematic of the cell where the films were grown. The cell is made of two round quartz plates 1 and 2. Plate 1 is a lid. Plate 2 has a round trough 3 in the center and works as a container for a thin crystal. The trough is surrounded by a circular trench 4, which collects the excessive material during melting process. The plates have on their inner surfaces ITO electrodes 5 and 6. Gold wires 7 and 8 are attached to the electrodes on opposite sides of the cell. Parameter *d* is the depth of the trough and correspondingly the thickness of the film. In our experiments we varied *d* from 2 to 10 microns. The cell was mounted into a chamber heated by pumping high temperature heat carrier liquid SYNTHERM 800 with a high temperature circulator. The chamber was placed on a stage of a polarizing optical microscope. This was done in order to monitor continuously the state of the growing crystal. Initially, polycrystalline powder of NPP was put in the trough. Plate 2 was then heated. When the material melted down, plate 1 was mounted. The excess of the melted material was collected in the trench. Then the film was let to cool down. The material

showed dense polycrystalline structure when observed under the microscope with crossed polarizers. In our system the temperature in the middle of the trough was maintained lower than that at the edges. It made possible to choose a proper seed located in the middle while melting all the crystallites in the peripheral regions. We heated the cell and cooled it down multiple times until we had only one seed in the middle with the rest of the material in the melt. The melt was observed in the microscope as a dark uniform region while the seed was seen as a uniformly illuminated faceted single crystal. Finally, by slow cooling we let the single crystal grow from the melt using the selected seed. Microscope photographs of different parts of a typical single crystal film are presented in Fig. 2. Fig. 2a shows a region consisting of long uniform stripes separated by parallel cracks, and Fig. 2b demonstrates a region with relatively wide uniform area (about 0.36×0.68 mm^2). The size of the latter one is big enough for a laser beam (of 0.5 mm diameter) to pass through it without significant scattering.

2-2. Characterization. We characterized E-O properties of thin film samples of NPP using an improved version of the a.c. modulation method proposed by Yoshimura.[9] In this technique characterization could be done with relatively low (of the order of 10 V) a.c. voltage applied to the sample. The experimental setup for characterization of E-O properties of thin film organic crystals in longitudinal mode is shown in Fig. 3. A 35-mW He-Ne laser provides linearly polarized light beam at a wavelength of 633 nm. Mirror M directs the beam to the sample. Then the beam runs through polarizer P_1, the cell with the sample (10-μm thick film of NPP), and polarizer P_2. The cell is mounted on a holder with six degrees of freedom: three translations and three rotations. This provides flexibility in orientation of the sample with respect to the incident light beam. Optical fiber transmits the output light to a photo detector. An a.c. voltage with maximum amplitude of up to 24 V from a signal generator is applied to the electrodes of the cell. The signal from the photo detector is processed by a lock-in amplifier, which is synchronized by the signal generator. An oscilloscope monitors the signal from the photo detector.

Experimental characterization of the E-O properties starts from determining the orientation of dielectric axes. It has been previously suggested that dielectric axes x and y laid in, and z was normal to the plane of the film. Theoretical analysis shows that if the

two-fold axis y is within the plane of the film, the longitudinal linear E-O effect does not exist. However, our preliminary measurements showed an unexpectedly strong longitudinal linear E-O effect. Thus the two-fold axis y more likely laid off the plane of the film. We also observed a drop of the intensity of the transmitted light ("dark field") when the sample placed in a polarizing microscope between crossed polarizers was rotated until the cracks became parallel to the polarization direction of either polarizer. We believe that cracks were likely close to the direction of dense packing in the crystal, which must coincide with axis x, since refractive index n_x is the highest in NPP. The observation of the "dark field" additionally suggested that this was the case. If the crystal is oriented with axis x parallel to either polarizer, the light passing through it remains linearly polarized along the direction of the input polarizer and thus can not pass through the cross-oriented output polarizer. The two above-mentioned experimental facts allowed us to assume that even if the plane made by the pair of axes x and y laid off the plane of the film, the tilt was not substantial. In other words, the angle between axis z and the normal to the film was more likely of the order of few degrees. In fact, our detailed investigation showed that this angle was only 5.2^0, and the maximum of the E-O effect had to be observed when the light propagated along z. Accordingly, in further description of the experimental approach we always assume that the film is tilted to the optimum position when the propagation direction of the light is parallel to z. This configuration is shown in Fig. 4. The angle between axis z and the normal to the film w is denoted as ξ. The projection u of axis x on the plane of the film is parallel to the cracks. During observations of the E-O effect polarization direction P_2 of the output polarizer was always kept at an angle of 90^0 with respect to polarization direction P_1 of the input polarizer. The angle between axis x and P_1 is denoted as θ.

2-3. Electro-optic modulator (Fig. 5). The principle of operation of the device is the following: light from a laser (TE or TM polarized) is injected into a film of electro-optic material made of single organic crystal. The film is thick enough to support two propagating modes of the 0-th and the 1-st order. A focusing lens is used to excite the two modes simultaneously. There is an optical isolation layer between the point of injection and the point of light decoupling. This isolation layer is inserted in the prism and has refractive index lower that the index of the film. The index of the coupling prism should

be higher than the index of the film. At a certain incidence angle θ_m a waveguide mode of the m-th order with propagation index N_m could be excited. The function is determined by the dispersion equations. For p-polarized light the 0-th order mode is actually a surface plasmon, a highly attenuated excitation localized on the interface between the metal prism coating (gold or silver) and the nonlinear organic film. If the film is thick enough (a few microns), and has good optical quality and low absorption at the wavelength of the incident light, then at greater angles θ_m low loss propagating modes of the film could be excited. By scanning the incidence angle one can actually observe sharp dips in the signal reflected from the prism in the vicinity of each θ_m due to extraction of energy from the beam and its conversion into the energy of the m-th mode.

The metal-coated substrate is also separated from the film with a dielectric layer with refractive index lower than that of the film. Even if the substrate has itself a refractive index lower than the index of the film, this additional dielectric layer is an option, which reduces losses of the propagating light due to presence of the metal electrode. Optical isolation provides light confinement within the film thus making it a planar waveguide for the injected light. The position of the injection point with respect to the optical isolation layer of the prism is chosen such that the maximum energy of light is injected into the film without being decoupled back into the prism. The isolation layer actually eliminates decoupling. The length of the isolation layer is equal to the length L of interaction of the light with electro-optic material.

A trihedral prism is a conventional one used to couple light into a waveguide. The same type of prism is used to guide the light out of the film. Our approach in single crystalline film fabrication using the PG method makes one to assume another shape of the prism, namely, a prism of C_∞ symmetry. We have explored prisms of different shape, technological approach in preparation of dielectric and conducting layers. We have obtained promising results with these prisms, and we still continue our efforts to optimize the modulator, which comprises our traditional cell and a prism as a lid and waveguiding element. In addition, application of a prism as an element for waveguiding provides an unique opportunity to combine longitudinal and transverse approach in obtaining electro-optical effect.

2-4. Materials Studied. We have concentrated our efforts on following organic materials with significant electro-optical coefficients:

- 2-methyl-4-nitroaniline (MNA),
- 4'-dimethylamino-N-methyl-4-stilbazolium methylsulfate (SPCD),
- 2-cyclooctylamine-5-nitropyridine (COANP),
- 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium tosylate (DAST),
- N-(4-nitrophenyl)-L-prolinol (NPP),
- 2-(N-prolinol)-5-nitropyridine (PNP),
- (-)2-α-(methylbenzylamino)-5-nitropyridine (MBANP), and
- Lithium Niobate ($LiNbO_3$).

The DAST compound had been reported to have the highest electro-optic coefficient [10], but we did not succeed with crystal growth of this material. The compound decomposed at the melt temperature. The most attractive compound we found to be was NPP. We found that NPP reveal the highest electro-optical coefficient, and what is more curious is that we observed the size effect (thickness of the film) on electro-optical performance. This was the reason that we concentrated our efforts mostly on NPP. Lithium niobate electro-optics studies were conducted for comparison with the rest of materials.

2-5. Results and discussion.

2-5-1. *Half-wave voltage.* Fig. 6 shows a typical oscillogram of the intensity of light passing through the NPP film (solid curve) with an a.c. voltage applied to it (dashed curve). The peak-to-peak value of a.c. voltage was 18 V. The response of the sample is a periodical signal with a frequency of the a.c. voltage. Fig. 7 shows the amplitude I_Ω of the intensity versus the peak-to-peak value of the a.c. voltage V_0 at a frequency of 82.0 kHz. The plot clearly shows a significant linear longitudinal E-O effect in the film. For this experimental data set, we have $\theta = 46^0$, $I_c = 34.2$ mV. By using the same method of Yoshimura, we found that $\delta_c = 80^0$, and half-wave voltage $V_\pi =$ (3.24 ± 0.06) kV. Fig. 8 displays in logarithmic scale both the amplitude of the fundamental I_Ω and second harmonic $I_{2\Omega}$ of the intensities of the transmitted light plotted as functions of the amplitude of the a.c. voltage. Using the estimated value of V_π we

calculated the figure-of-merit $F = (99.2 \pm 3.4)$ pm/V, which compares with that of lithium niobate (about 120 pm/V).

2-5-2. *Electro-optic coefficients.* According to Ref. 3, E-O coefficient $r_{12} \approx 3r_{22}$. Taking into account previously estimated V_π and ξ, we found coefficients r_{12} and r_{22} to be 461 (pm/V) and 154 (pm/V) respectively. These values are much higher than those in Ref. 3. One of the reasons could be the presence of a high internal electric field in the crystal produced by a substantial stress via the conversed piezoelectric effect. The cracks give some evidence to this stress because here they give some release to it. Another explanation could be that light propagating along the cracks is collimated between the cracks thus switching on the Čerenkov mechanism. This phenomenon is to be explored.

2-6. Conclusions

We developed the plate-guided method of growing single crystal films of NPP with uniform areas as large as 0.25 mm^2. The half-wave voltage of the longitudinal E-O modulation and the figure-of-merit were obtained by using the a.c. modulation technique. The orientation of the dielectric axis z was determined by measuring the maximum amplitude of the modulated intensity of the transmitted light when varying the incidence angle of the light beam. The E-O coefficients r_{12}, r_{22} have been evaluated as 461(pm/V) and 154 (pm/V) respectively. Thin single crystal films of NPP appear to be suitable to various applications such as longitudinal E-O modulators (for example, in configuration of Fabry-Perot interferometer) and optical switches.

2-7. Students' defense.

During the report period, two students defended their theses. Mr. Javier Wu defended thesis "Nonlinear Optical Properties of Organic Thin film Materials" on July 5, 2000 and received Degree of M.Sc. Mr. Wu continues his studies in the Ph.D. program of the University of Puerto Rico, Rio Piedras Campus. A copy of his thesis could be obtained by request from the General Library of University of Puerto Rico, Mayaguez Campus, PR 00680. Mr. Zhifu Liu defended his doctoral dissertation "Fabrication and Characterization of Electro-optic Organic thin film Modulators" on June 29, 2001, and

received Ph.D. Degree. At present, Dr. Zhifu Liu works in Industry. His dissertation could be obtained from the AAMU Library, Normal, AL 35762.

2-8. Participating people.

The following people participated in conducting and/or discussing the results of the project:

1. Dr. Alexander Leyderman, PI
2. Dr. Sergey Sarkisov, Co-PI
3. Dr. Michael Curley, Post Doctoral Fellow
4. Dr. Nickolai Kukhtarev, Visiting Scientist
5. Dr. Valentine Vikhnin, Visiting Scientist
6. Prof. Shi-Xian Qu, Visiting Scientist
7. Dr. Yunlong Cui, Post Doctoral Fellow
8. Mr. Zhifu Liu, Graduate Student
9. Mr. Javier Wu, Graduate Student
10. Ms. Aisha Fields, Graduate Student
11. Mr. Okedi Omereji, part time U/G Student
12. Mr. Ramon Diaz, part time U/G Student.

2-9. Publications stemming from the Project

1. A.Leyderman, Y.Cui, J.Wu, S.Sarkisov, M.Curley, Curtis Banks, Benjamin Penn "Growth and characterization of single crystal organic thin films for electro-optics modulators", *SPIE-99,* **3793,** 45-54 (1999).
2. Zhifu Liu, Sergey S. Sarkisov, Michael J. Curley, Alexander Leyderman, Yunlong Cui, Javier Wu , "Diagnostics and growth of organic thin films for electro-optic modulators with low driving voltage", *SPIE Int. Optical Devices and Diagnostic of in Materials Science* , **4098,** 40-51 (2000).
3. Zhifu Liu, Sergey S. Sarkisov, Michael J. Curley, Alexander Leyderman, Javier Wu, Charles Y. Lee, Electro-optic modulators based on organic single crystal films, *SPIE Int. Optical Devices and Diagnostic of in Materials Science* , **4461,** # 37 (2000)
4. Zhifu Liu, S.S. Sarkisov, M.J.Curley, A.Leyderman, Yunlong Cui, and J.W. Li, B.G.Penn "Longitudinal electro-optic effect in single crystal films of N-(4-nitrophenyl)-(L)-prolinol (NPP)", *JOSA B* , Submitted.

2-10. Inventions

1. Alexander Leyderman, *Organic Crystalline Film Device for Optical Applications and Related Methods of Fabrications,* Patent #6,198,530, Issued March 6, 2001.

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1. J. Badan, R. Hierle, A. Perigaund, and J. Zyss, ACS Symp. Ser. **233**, 81-107 (1983).
2. G. F. Lipscomb, A. F. Garito, and R. S. Narang, "An exceptionally large linear electro-optic effect in the organic solid MNA," J. Chem. Phys. **75**, 1509-1516 (1981).
3. Jianjun Xu, Ligui Zhou, and M. Thakur, "Measurement of electro-optic effects in single crystal films of N-(4-nitrophenyl)-L-prolinol," Appl. Phys. Lett. **69**, 1197-1198 (1996).
4. A. Leyderman, M. Espinosa, T. Timofeeva, R. Clark, D. Frazier and B. Penn, "Growth and characterization of crystalline films of meta-nitroaniline (mNA) and 2-cyclo-octylamino-5-nitropyrydine (COANP)," in *Space processing of materials*, N. Ramachandran, Ed., Proc. SPIE **2809**, 144-154 (1996).
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6. A. Leyderman, US Patents ## 5746823 & 5716823.
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9. T. Yoshimura, "Characterization of the electro-optic effect in styrylpyridinium cyanine dye thin-film crystals by an ac modulation method," J. Appl. Phys. **62**, 2028-2032 (1987).
10. F. Pan, G. Knopfle, Ch. Bosshard, S. Follonier, R. Spreiter, M. S. Wong, and P. Gunter, "Electro-optic properties of the organic salt 4-N, N-dimethylamino-4'-N'-methyl-stilbazolium tosylate," Appl. Phys. Lett. **69**, 13-15 (1996).

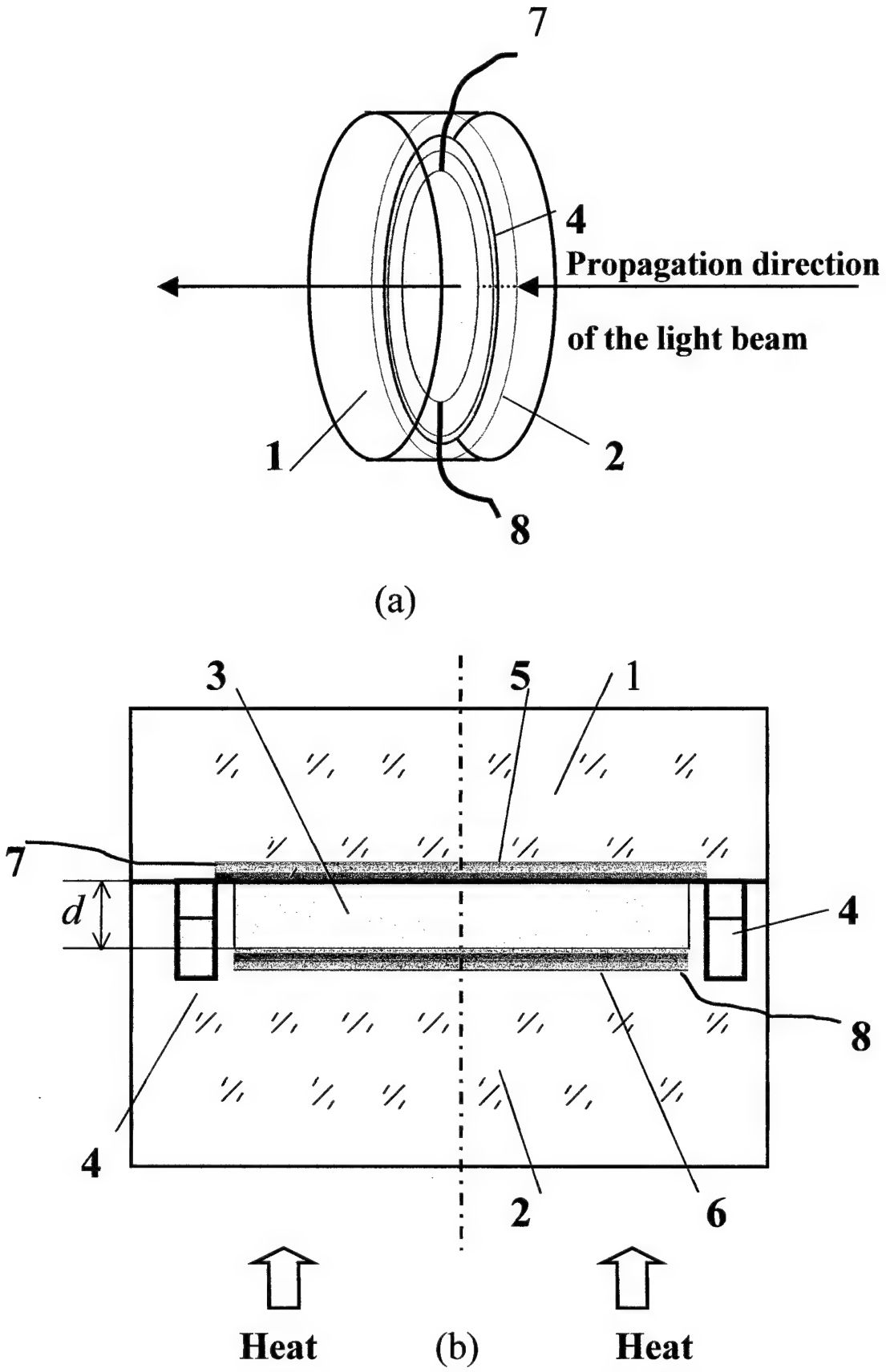
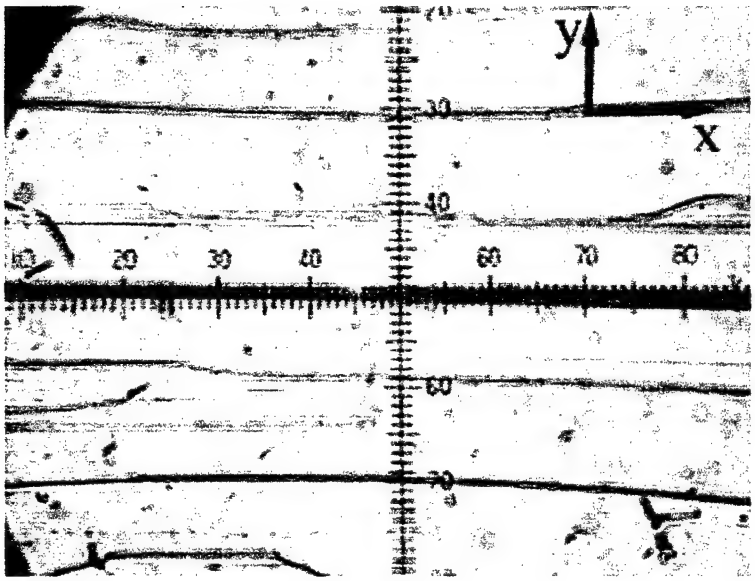
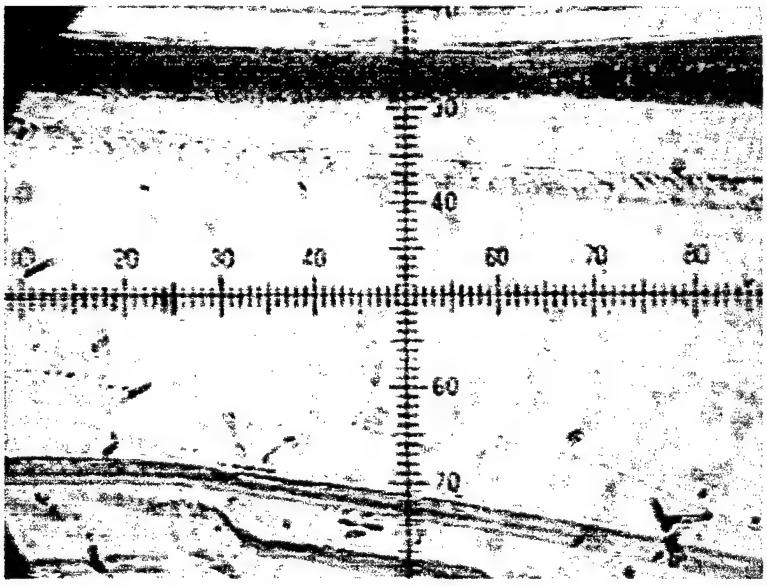


Fig. 1. Schematic of the cell where thin crystalline film of NPP was grown. The cell is shown (a) as oriented with respect to the light beam and (b) cross-sectional view.



(a)



(b)

Fig.2. The microscope photograph of(a)region of NPP single crystal with parallel strips; (b) region with relatively wide uniform areas. The size of the main scale unit in the photographs is 90 um.

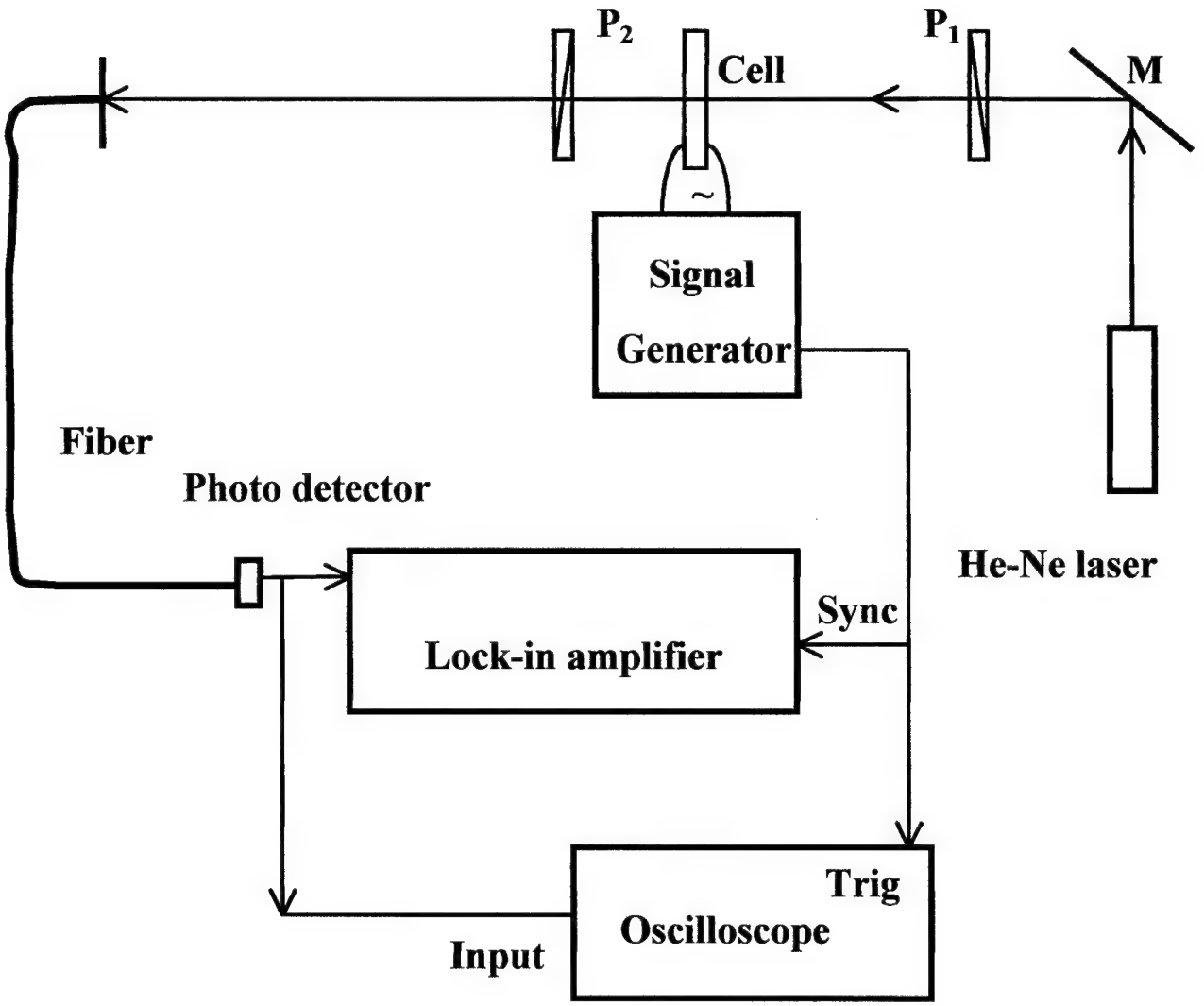


Fig. 3. Experimental setup for characterization of E-O properties of thin film samples. M-mirror, P_1, P_2 are polarizers.

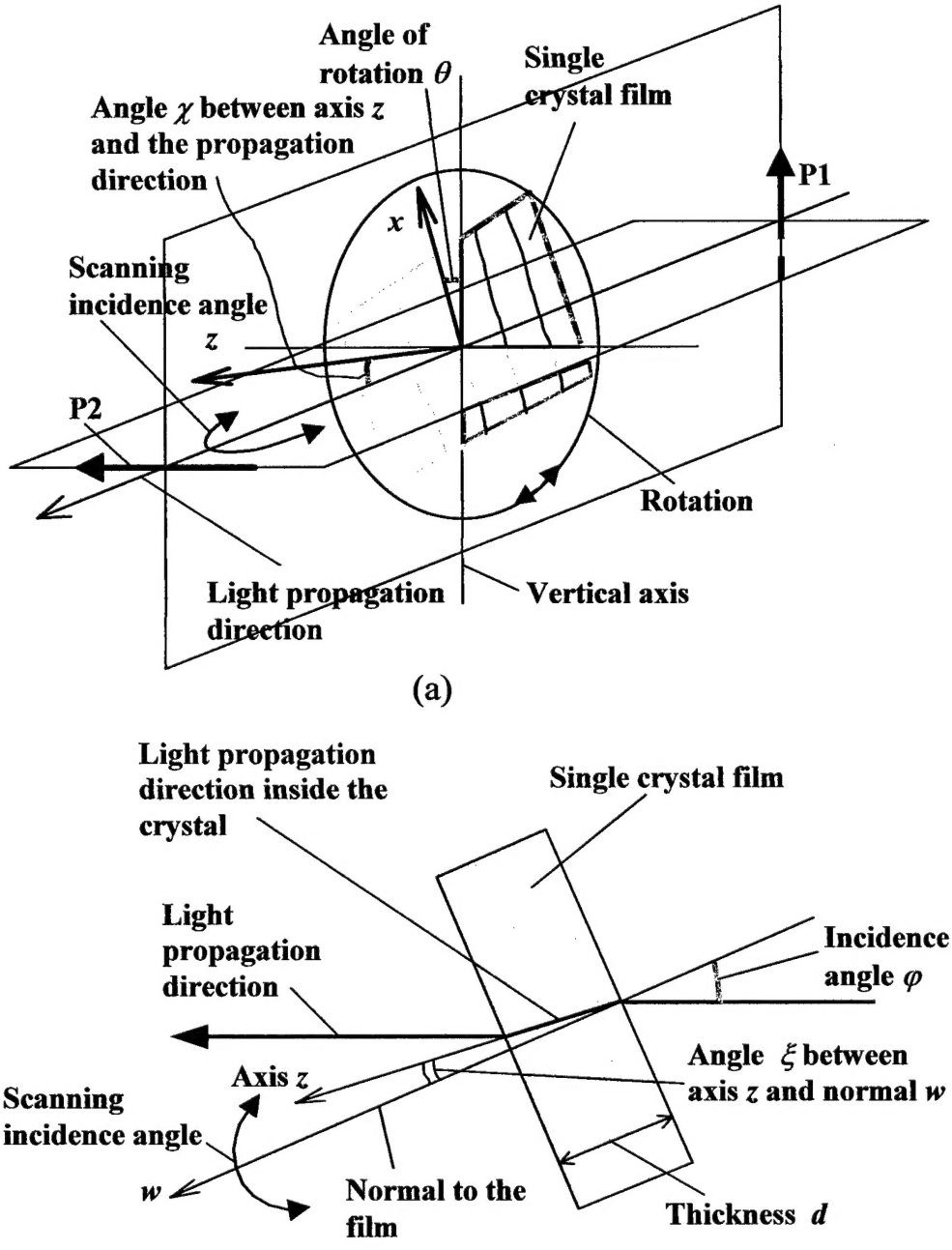


Fig. 4. The configuration of the polarization directions of input and output polarizers P_1 and P_2, respectively, and the orientation of the optic axes of the crystalline film of NPP. E is the optic field after passing polarizer P_1. a-the light beam is perpendicular to the page, b-the light propagates in the plane of the page.

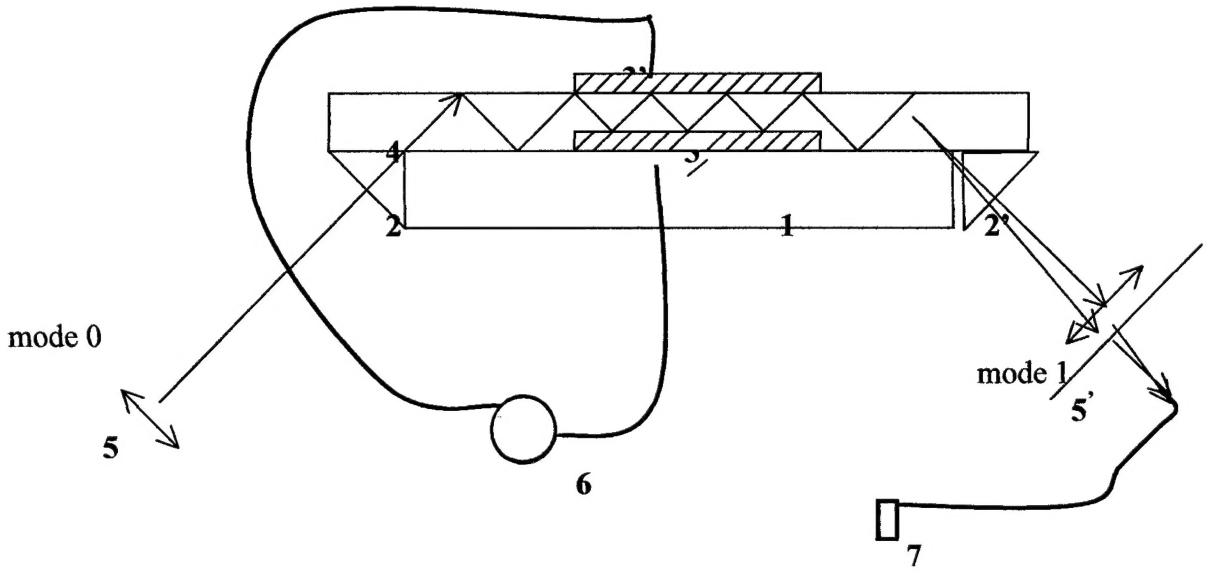


Fig. 5. Thin film waveguide E-O modulator integrated with coupling prisms. 1 is the fused quartz substrate, 2 and 2' are the high index glass prisms, 3 and 3' are conducting layers, 4 is the organic thin film, 5 and 5' are lenses, 6 is the modulating signal, 7 is the detector.

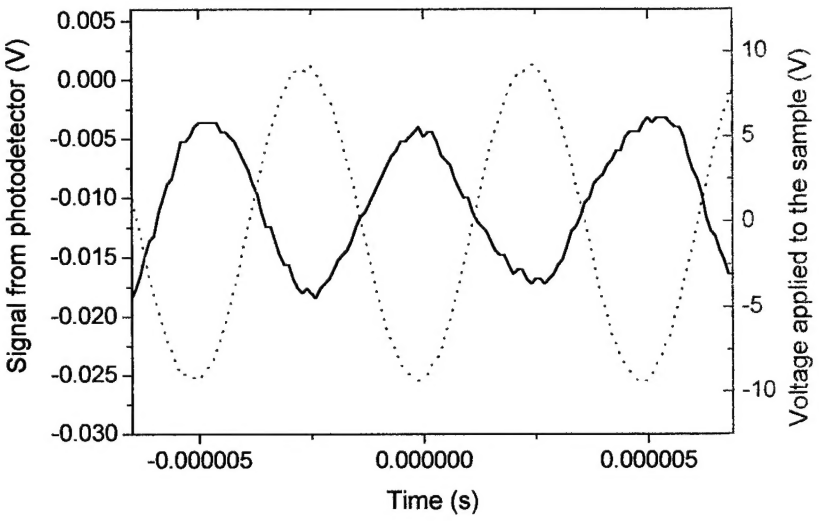


Fig. 6. The response of the NPP sample (solid curve) to the a.c. voltage (dotted curve) as measured by the photo detector at 200 kHz.

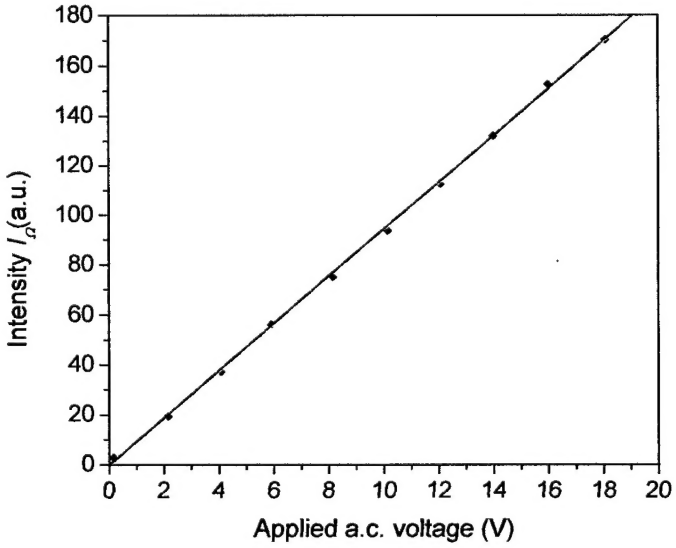


Fig. 7. The amplitude of the signal from the photo detector amplified by the lock-in amplifier versus the amplitude of the a.c. voltage applied to the NPP sample at a frequency of 82.0 kHz. The solid line is linear fitting of the experimental data.

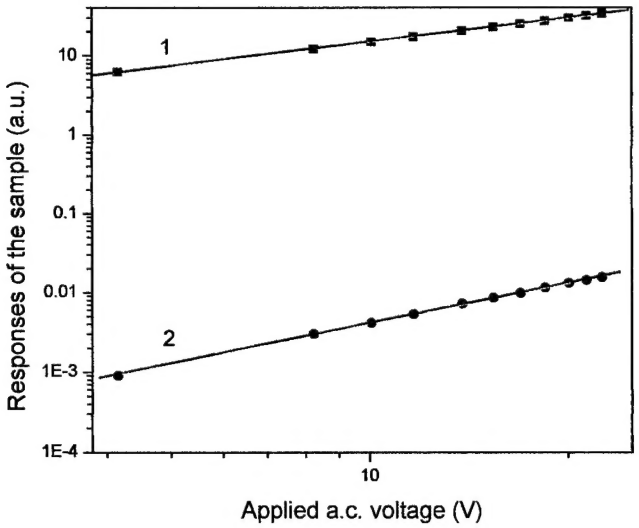


Fig. 8. The fundamental frequency (13.5 kHz, solid square) and the double frequency (solid circle) responses of the sample with respect to the a.c. voltage.